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Evaluation of Calcium Sensors in Fresh- and Saltwater

Interagency Energy/Environment R&D Program Report

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16. ABSTRACT

The Orion Calcium Ion Electrode #93-20 was evaluated for suitability as a calcium ion sensor for monitoring or in-situ marine applications by testing for the following parameters: accuracy, precision, temperature dependence, short - and long-term stability, durability, sensitivity to fluctuations in light intensity and flow conditions, response time as a function of temperature and concentration, and variability between modules. The tests were performed at 10°C and 25°C in freshwater, synthetic seawater and natural waters (35-, 20- and 5ppt salinity). A description of the sensor, theory of operation and a summary of the test results are included. The electrode response for two of the detectors was a linear function of the calcium concentration. All three detector-modules failed before the end of the 6 month warranty period. Although the accuracy in high salinity samples (>20-ppt) was poor, the concentration measurements were accurate to better than 7% in low salinity seawater, indicating a susceptiblity of the sensor to a "salt extraction effect" which results in electrode drift and inaccuracy in salt solutions. The long response times (i.e., average of 33 minutes in freshwater) and sensitivity to flow conditions would make the application of this calcium sensor to in-situ measurements very difficult.

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EVALUATION OF CALCIUM SENSORS IN FRESH- AND SALTWATER

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FOREWORD

The Test and Evaluation Laboratory of the National Ocean Survey's Office of Marine Technology, National Oceanic and Atmospheric Administration, conducts work to:

- test and evaluate new or state-of-the art sensors for use in the marine environment
- determine the error bounds on chemical sensors' performance to obtain data quality assurance information
- determine suitability of new sensors for in situ or field use
- evaluate new methods for the chemical analysis of seawater
- develop standards and calibration equipment and procedures to maintain a quality assurance program for measurements in the marine environment.

New chemical sensors are under continual test and evaluation to assure that the most accurate results possible are obtained. If specific ion electrodes are to be used to measure chemical parameters in seawater, they must be evaluated directly in the medium of interest, i.e., seawater. This report investigates the basic characteristics of specific ion electrodes in a variety of water types to determine their suitability for in situ or monitoring applications.

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ABSTRACT

The Orion Calcium Ion Electrode #93-20 was evaluated for suitability as a calcium ion sensor for either monitoring or in situ marine applications. The electrode was tested with three separate sensor modules for the following parameters: accuracy, precision, temperature dependence, short- and long-term stability, durability, sensitivity to fluctuations in light intensity and flow conditions, response time as a function of temperature and concentration, and variability between modules. The three sensors of the "liquid ion-exchange" type were evaluated at 10°C and 25°C in freshwater, synthetic seawater (35-, 20-, and 5-ppt salinity), and natural waters (IAPSO standard seawater, Atlantic Ocean water, and Chesapeake Bay water). A description of the sensor, theory of operation, and a summary of the test results are included. The electrode response for two of the modules was a linear function of the logarithm of calcium concentration. All three modules failed prematurely (i.e., before the 6-mo guaranteed period). While the accuracy in high salinity samples (35 and 20 ppt) was poor, the concentration measurement was better than 7% in 5-ppt salinity seawater and indicates a susceptibility of the sensor to the "salt-extraction effect," which results in electrode drift and abnormal inaccuracy in salt solutions. The long response times (i.e., average of 33 min in freshwater) and sensitivity to flow conditions make the practical application of this calcium sensor to in situ measurements a somewhat dubious proposition.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ACS	--	American Chemical Society
cm	--	centimeter
h	--	hour
IAPSO	--	International Association for the Physical Sciences of the Ocean
ISA	--	ionic strength adjustor
log	--	logarithm
min	--	minute
ml	--	milliliter
mV	--	millivolt
ppt	--	parts per thousand
RSE	--	residual standard error
sat'd	--	saturated

SYMBOLS

A	--	activity
Ag^+	--	silver ion
°C	--	degrees Celsius
Ca^{2+}	--	calcium ion
E	--	electrode potential
E°	--	electrode constant
F	--	Faraday's constant
I	--	ionic strength
°K	--	degrees Kelvin
KCl	--	potassium chloride
M	--	molarity
R	--	universal gas constant
S	--	electrode slope
T	--	temperature
T_1	--	response time within 1 mV
T_{95}	--	95% response time
z	--	ionic charge
γ	--	activity coefficient
σ	--	standard deviation
$\sim$	--	approximately

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SECTION 1

INTRODUCTION

Recently developed ion-selective electrodes have received considerable attention in the past few years for a variety of applications. Their selectivity, simplicity, and low cost make these sensors attractive devices for water quality measurements in a wide range of natural waters. Although ion electrodes are available for many chemical species, little work has been done on the performance and characteristic behavior of the sensors in media other than pure water (e.g., in seawater). The accuracy, precision, and reliability must be known before they can be used for meaningful measurements.

The Orion Calcium Ion Electrode can theoretically be used to measure directly the calcium activity in seawater or freshwater without sample pretreatment and thereby becomes a candidate for in situ application in water quality measurements. Since calcium is a major constituent of seawater, the element has been the subject of many studies in the marine sciences due to the involvement of calcium in many biological, geological, and chemical processes in the oceans.

In this study, the Orion Calcium Ion Electrode #93-20 was evaluated for its performance and accuracy in samples from freshwater, estuarine, and seawater environments.

SECTION 2

CONCLUSIONS

(1) The sensor modules failed to operate for the entire "6-month" period guaranteed by the manufacturer even though they were used well before the "expiration date." They generally lasted only about 3 months. Since the sensors have a relatively short shelf life, it took a significant amount of time to obtain replacements from manufacturers.

(2) The electrodes are physically durable since the body is made of hard plastic.

(3) The height of the filling solution in the reference electrode had no effect on the electrode potential as long as it was above the sample solution (required to maintain a positive pressure).

(4) The amount of available light had no effect on the sensors.

(5) While two sensors had a linear response in freshwater, one sensor required a 2d-degree calibration curve. All modules tested had a linear response in seawater.

(6) Although the calibration curves in some cases were linear, the residual standard error (scatter about the curve) indicates that at least a three-point calibration is required to obtain useful results.

(7) The reproducibility of $\pm 4\%$ (± 0.5 mV) claimed by the manufacturer only holds if the sensor is calibrated hourly. Since the response times were quite long (average of 33 min and 18 min in freshwater and seawater, respectively), this specification was difficult to check directly, and in light of the response times is rather meaningless. However, the sensor drift from Table 5 does indicate the change in electrode potential over the 1-hour time period. In Evaluation #1, the average drift was a total of 0.8 mV/h (± 0.4 mV/h) and therefore, for these two sensors the specifications are correct. The sensor in Evaluation #2 with an average drift of ± 0.9 mV/h ($\sim 6\%$), did not meet the specifications.

(8) The results indicate that the calcium electrode should not be used in freshwater without an ionic strength adjustor (ISA). Direct measurements with some sample pre-treatment is possible only in low salinity (5 ppt) seawater. The accuracy at higher salinities was too poor for reliable results to be obtained with the electrode, even if the sensor is calibrated in synthetic seawater solutions. For this reason, the calcium electrode is generally unsuitable for direct in situ measurements in the marine environment. The sensor could be used in conjunction with some type of sample pre-treatment and frequent multi-point calibrations, but its sensitivity to flow variations and long response time would not make these electrodes easily adaptable to continuous monitoring applications.

SECTION 3

EXPERIMENTAL PROCEDURE

INSTRUMENT DESCRIPTION

The Orion Calcium Ion Electrode #93-20 was manufactured by Orion Research, Inc., with the specifications given in Table 1. The electrode is the liquid ion-exchange type with a replaceable sensor module (see Figure 1), similar to the Orion Divalent Ion Electrode, (Ward, 1978a), and is described in further detail in the Appendix. The Model #93-20 sensor replaces the older Orion #22-20 electrode and requires an external reference electrode to measure calcium in aqueous solutions. The reference electrode used in this study was the Orion #90-91 Single Junction Reference electrode with the Orion #90-00-11 Filling Solution (4M KCl sat'd with Ag^+) as recommended by the manufacturer. The reference electrode was the "sleeve" type and is described in detail elsewhere (Ward, 1978b).

TABLE 1. MANUFACTURER'S SPECIFICATIONS

Concentration range	8×10^{-6} to 1M
pH range	5.5 to 11 pH
Temperature range	0° to 50°C
Electrode resistance	1 to 4 megohms
Reproducibility	±4%
Sample	aqueous solutions only
Minimum sample size	3 ml in a 50-ml beaker 0.3 ml in Orion Microsample Dish (Cat. No. 92-00-14)
Storage	store in air
Module life	6 months under normal laboratory conditions
Size	electrode length: 13.5 cm diameter: 1.1 cm cap diameter: 1.6 cm cable length: 75.0 cm

The electrode potential developed by the electrode system was measured with an Orion Model 801A Digital pH/mV Meter with a range of ±1999.9 mV in 0.1 mV increments and with a repeatability of ±0.1 mV. The meter features a high input impedance, extremely low drift, and an output display directly in mV. The meter drift was less than 0.2 mV over a 6-month period.

The electrode was secured in the top of a polypropylene container, which was submerged in a well-insulated constant-temperature bath controlled to ±0.01°C. The sample container was sealed to prevent sample evaporation, and the bath was constructed to eliminate possible electrical ground loops or interferences which frequently plague electrode measurements. The sensor was kept at a constant 4 cm below the surface of the solution, which was agitated with a Teflon star-head magnetic stirring bar and a Troemner variable-speed submersible stirrer. The temperature was monitored constantly with a Hewlett-Packard quartz-crystal thermometer that was periodically calibrated against a platinum resistance thermometer. The sample solutions were suspended in the temperature bath immediately prior to each run to eliminate possible electrode response to temperature equilibration.

The salinities of the seawater samples were measured with a Guildline Model 8400 Laboratory Salinometer (AutoSal) which has been described in detail elsewhere (Boyd, 1976). The natural seawater samples were also analyzed for calcium with a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer. The calibration curves and fits were determined by a least-squares method with a Hewlett-Packard 9825A Programmable Calculator.

The freshwater standard solutions were prepared for Fisher Certified ACS Reagent Grade calcium chloride and Fisher Certified Atomic Absorption Standard Calcium Reference Solution. The synthetic seawater solutions were also prepared from Fisher Certified ACS Reagent Grade chemicals using the formula of Kester (1967). The 20- and 5-ppt salinity synthetic seawater were prepared from the 35-ppt seawater by weight dilution with pure water. The natural seawater samples were: (1) IAPSO standard seawater (P_{66} 27/7, 1974 - Cl = 19.3675) at 35-,20-,and 5-ppt (from weight dilutions); (2) Atlantic Ocean water (32.2-ppt salinity from 38° 40.3'N, 74° 20.0'W) at 32-and 20-ppt salinity (also diluted with pure water); and (3) Chesapeake Bay water at 4.2-ppt salinity. All dilutions were made with Millipore ion-exchanged (18-megohm) water.

TEST PROCEDURE AND RATIONALE

The electrodes were evaluated with three separate sensor modules (see Figure 1) at 10°C and 25°C in five different water types: pure water, synthetic seawater, IAPSO standard seawater, Atlantic Ocean water, and Chesapeake Bay water. The pure water tests were performed to establish basic electrode characteristics without chemical interferences and only slight ionic strength effects. The sensor was calibrated with synthetic seawater to determine the electrode performance in a complex solution of known composition that simulated natural seawater and its matrix effects. The subsequent electrode measurements in 35-,20-,and 5-ppt salinity IAPSO

seawater were made to determine the electrode accuracy after proper calibration with synthetic seawater standards and to observe the effect of salinity variations on the electrode response without relative compositional changes. Measurements were made in unpolluted Atlantic Ocean water to determine variations in electrode response between IAPSO seawater (treated Atlantic Ocean water) and natural untreated ocean water. Finally, the Chesapeake Bay water provided samples with an estuarine matrix and possible pollutant interferences.

The calibration curves in freshwater were obtained by measuring the calcium activity in standard solutions ranging from 0.1 M to 1 x 10^{-3} M - Ca^{2+}. Two consecutive runs were made at 25°C: the first in decreasing concentration step-changes, the second in increasing concentration steps. With this procedure the effects of directional concentration steps could be determined for response times, electrode calibrations, and reproducibility (short-term drift). The electrodes were subsequently calibrated at 10°C and then again at 25°C in the same standard solutions as the other runs. From these tests, the effects of positive or negative temperature variations could be measured for time response, calibration curves, electrode slopes, long-term drift (between the two 25°C runs), and durability to temperature changes. In each calibration run, the sensor was tested for: (1) short-term drift (3 hours); (2) sensitivity to flow variations; (3) sensitivity to changes in ambient light; (4) response due to motion of the electrode and wire connections; (5) variations in electrode potential due to different filling-solution heights; and (6) electrode response as a function of time.

The calibrations in synthetic seawater were performed by measuring the calcium activity in four standard seawater solutions of known calcium content at the same salinity as the natural water samples. Immediately after calibration, the values for calcium activity were determined in two different natural water samples. Since the relationship of activity to concentration is not accurately known in seawater (see Appendix), the test results and calibration curves were calculated in concentration units. This procedure was completed at 35-, 20-, and 5-ppt salinity.

The concentrations of calcium in the natural waters were determined from atomic absorption spectrophotometric measurements. From the seawater runs, we ascertained the effect of salinity on the electrode potential and response times, the stability and accuracy in various water types, sensitivity to variations in light intensity, and suitability for possible in situ monitoring in freshwater, estuarine, and seawater environments.

SECTION 4

RESULTS

CALIBRATIONS

Three evaluations were performed with three separate sensor modules. The first module, one of two supplied with the electrode body, failed after 2.5 months. The second module, also supplied with the electrode, was then assembled and the tests resumed (Evaluation #1). Toward the end of the tests, the second module became unstable, and a new replacement module was ordered. When the new sensor was received, Evaluations #2 and #3 were completed. The low slopes found in Evaluation #3 indicate that this module was also beginning to fail, although all three modules were used well before the expiration date stamped on the module container.

At least seven calibration runs were performed during each evaluation: four in freshwater at 10°C and 25°C, and three in seawater at 35-, 20-, and 5-ppt salinity. The sensors were assembled and soaked in 0.1 M $CaCl_2$ for 2 days prior to the tests. All concentrations are given in molarity (M) defined as the moles of calcium (Ca^{2+}) per liter of solution.

The potential developed by the electrode system was remarkably different between sensors in the same calcium standard solution at the same temperature. At 25°C, for example, in a 0.1 M Ca solution, potentials of 64.8, 78.4, and -175.1 mV were recorded with three separate modules against the same reference electrode. Obviously, the absolute value of the electrode potential is very dependent on the individual characteristics of each module and can only be determined empirically by calibration in standard solutions.

The calibration curves for the Orion Calcium Ion Electrode in freshwater at 25°C are shown in Figures 2-4, where the electrode potential (mV) is plotted versus the logarithm of the Ca^{2+} concentration. Theoretically, the electrode response should be a linear function of log M with a slope of around 27 mV/decade at 25°C. The response of the first module in freshwater, however, was not a linear function of log M (see Figure 2), and therefore the electrode potential had to be fitted to the equation:

$$E = E^\circ + S \log M + B (\log M)^2 \qquad (1)$$

rather than the modified Nernst equation:

$$E = E^\circ + S \log M \qquad (2)$$

where E is the electrode potential in a solution of M in calcium concentration, E° is a constant (intercept), S is the slope, and B is an empirical "deviation" coefficient. The values for E°, S, and B are given in Table 2 for freshwater and seawater for Evaluations #1 to #3, along with the residual standard error (RSE) for the curve fits. Since the results from Evaluation #1 with the second module and from Evaluations #2 & #3 with the

third module appear to be linear with log M, the data for these sensors were therefore fitted to Equation (2), and the coefficients also tabulated in Table 2.

In Evaluation #1, the freshwater Runs #1-3 were performed with the first sensor module, which exhibited a nonlinear response with the log of calcium concentration (Figure 2). The second module (freshwater Run #4 and seawater runs in Evaluation #1) and the third module (Evaluation #2) had a linear response with the log M (Ca^{2+}) as shown in Figures 2 and 3. Although the sensor response in Evaluation #2 was more linear with concentration than that in Evaluation #1, the scatter about the fitted curves was significantly greater (higher RSE values).

In Evaluation #2, the large change in electrode slope observed between Runs #1 and #2 was considerably reduced. (See Figure 3 and Table 2.) This may be due to a "stabilizing" effect from the low temperature 10°C run, a characteristic that has been observed for other liquid ion-exchange electrodes (Ward, 1978b). In Evaluation #2, Runs #3 and #4 in freshwater were completed after the seawater measurements to show that the use in seawater media did not adversely affect the sensor. However, by the time Run #5 was completed, the electrode slope had decreased to only 4 mV/decade and the sensor response began degenerating rapidly. In Evaluation #3, the electrode slope decreased until, finally, negative values was observed. Apparently, the life of the sensor modules was somewhat shorter than the 6-months suggested by the manufacturer.

The effect of temperature on the calcium electrode response is shown in Figures 5 and 6 for Evaluations #1 and #2, respectively. The first module (Evaluation #1) was temperature sensitive (see Figure 5) in that the "deviation term," B, changed significantly while the slope term, S, remained nearly constant. In Evaluation #2, the considerable scatter in the data points for the first two runs made the comparison of the 25°C data to the 10°C results very difficult (Figure 6). The removal of "bad" points from Run #2 (error > 3 σ) resulted in the curve plotted in Figure 6 in which Run #2 has a slope similar to Run #1 in freshwater. The coefficients given in Table 2 reflect the uncorrected calibration curve and the values in parentheses are the corrected coefficients for which the RSE, by removal of bad data, was reduced by nearly one-third. The corrected linear curves indicate a decrease of 3 mV in the slope term between 10°C and 25°C. In Evaluation #3, the sensor was subjected to a second series of 10°C runs, at which time the slope term became negative, indicating a defective sensor.

The seawater calibrations for Evaluations #1 and #2 are shown in Figures 7 and 8 as a function of salinity and calcium concentration. Although the slope term changed significantly with salinity, both modules maintained a linear response with the logarithm of concentration. In both evaluations, the electrode slopes approached the Nernst theoretical valve as the salinity approached zero, indicating that the addition of a low ionic strength adjustor (ISA) would result in better measurements in freshwater. While the electrode slopes in pure water without pre-treatment were quite low, the values in low ionic strength solutions (5-ppt salinity

TABLE 2. COEFFICIENTS FOR CALIBRATION CURVES FOR ORION CALCIUM ELECTRODE

Water type	Run	E°	S	B	RSE
			EVALUATION #1		
Freshwater					
25°C	1	57.4	-35.98	-13.47	0.2
	2	55.8	-15.18	- 6.15	0.4
	3	59.5	-14.49	- 6.58	0.8
	4	89.0(86.9)	10.54(8.08)	- 6.27	1.7(2.3)
10°C	1	47.6	-15.05	- 5.16	0.1
Seawater					
5 ppt		100.7	19.66	---	1.2
20 ppt		87.7	16.59	---	0.9
35 ppt		84.4	13.11	---	0.2
			EVALUATION #2		
Freshwater					
25°C	1	-159.6(-156.9)	18.56(18.85)	---	2.5(5.2)
	2	-179.5(-160.1)	9.28(16.14)	---	0.7(4.5)
	3	-177.2	10.16	---	1.9
	4	-175.7	8.77	---	3.8
	5	-235.9	4.65	---	1.9
10°C	1	-170.6	13.54	---	0.8
Seawater					
5 ppt		-171.8	22.35	---	1.0
20 ppt		-186.3	17.38	---	0.9
35 ppt		-199.4	13.14	---	0.4
			EVALUATION #3		
Freshwater					
25°C	1	-194.0	4.19	---	1.5
	2	-200.2	-0.96	---	3.3
10°C	1	-208.9	-2.55	---	3.2

seawater) were much closer to the theoretical slopes. It is therefore recommended that the ionic strength of samples should be adjusted (as recommended by the manufacturer) to obtain reliable results. The ISA was not added to the freshwater samples in this study, because we were attempting to use the sensors directly in various water media without sample pre-treatment. Although ISA is required for freshwater measurements, the linear calibration curves in seawater suggest a possible application for oceanographic purposes where the ionic strength is usually constant and relatively high.

ACCURACY

The accuracy of the calcium ion electrode was determined in natural waters at 35-, 20-, and 5-ppt salinity by comparing the values for calcium concentration obtained with the Orion electrode to the values determined by chemical analysis on the atomic absorption spectrophotometer and by constant-composition salinity calculations. The electrode measurements of the calcium activity in the natural water samples were completed immediately after the sensor was calibrated with four standard synthetic seawater solutions of known calcium content at the same salinity as the test sample.

The electrode accuracy is given in Table 3 for Evaluations #1 and #2 as the percent error in calcium concentration, calculated from the electrode measurements, when compared to the "true" values obtained by the standard laboratory methods. The results from Evaluation #2 indicate that the electrode worked well in low salinity water with an accuracy of $\sim$ 6%. Above 5-ppt salinity, however, the measurement error increased substantially to $\sim$ 31%. Similar results were obtained in Evaluation #1, where the lowest error ($\sim$20%) was found at low salinity and the highest error ($\sim$48%) at high salinities. In both evaluations, the measurements in 32-ppt Atlantic Ocean water were worse than in the IAPSO water, because the electrode calibrations were sensitive to background salinity variations (see Figures 7 and 8), which could only partially be corrected. Since the sensors were calibrated in synthetic seawater solutions, the errors due to activity-concentration variations in the IAPSO samples should have been very small. The results, therefore, indicate that the calcium electrode cannot be used in high salinity samples without sample pre-treatment. As noted by the manufacturer, large deviations in electrode response can occur from a "salt-extraction effect" in which some salts in samples of high salt concentrations are extracted into the electrode membrane. Presumably, the salt extraction effect should have been eliminated by calibrating the sensor at the salinity of the sample. However, since this was not the case as found in our study, a better solution would be simply to dilute the sample down to a salinity of 5 ppt or less. This could easily be done in a monitoring mode in which the sensor could be calibrated with low salinity standards to give reliable results. Regardless of the reason, all the electrode readings in Evaluation #2 were low by 31% at 20-ppt salinity and higher, indicating that either the response was somehow suppressed or some part of the available calcium was tied up. If necessary, a purely mathematical factor of 31% could be used to compensate the values to the correct total Ca^{+2} concentration, resulting in accuracies of better than 8%.

TABLE 3. ACCURACY OF THE ORION CALCIUM ION ELECTRODE IN SEAWATER[a]

Salinity (ppt)	Water type	% Error[b]	
		Evaluation #1	Evaluation #2
35	IAPSO	40.8	31.9
	Atlantic Ocean	64.9	38.1
20	IAPSO	29.2	31.3
	Atlantic Ocean	32.4	31.3
5	IAPSO	20.5	6.2
	Chesapeake Bay	23.1	6.6

[a]The accuracy is given as the percentage of the difference in concentration from the true value.

[b]% Error = 100 x (observed - true)/true.

RESPONSE TIME

The response times are summarized in three different forms in this study: T_{95} (internal), T_{95} (external), and T_1 ($\pm$1 mV). The first two are the 95% response times and are defined as the time required for the system output to attain 95% of the asympotic value when subjected to a step input. The T_{95} term is equal to three "time constants" ($1-e^{-1}$) of a pure exponential response. The third time response T_1, is the time required for the sensor to reach a value within 1.0 mV ($\sim$7% in concentration) of the final electrode potential.

The electrode potential was monitored continuously for 3 hours in each test solution, starting from the moment the sensor was immersed. The T_{95} (internal), or $T_{95}(I)$, is the time required for the electrode response to reach 95% of the change between the initial and the final electrode potentials in one standard solution. The T_{95} (external), or $T_{95}(E)$, is the time required for the senor output to reach 95% of the change between the final potential in two consecutive test solutions at two different concentrations.

All three time responses are summarized in Table 4 and were obtained simply by averaging all the results in each individual run since the time responses in freshwater were independent of concentration level or direction of step-change. The T_1 time responses were considered to be the most useful parameters for evaluating the electrode equilibrium time since they were usually independent of the magnitude of the concentration step-change if the change was greater than 8%. All three methods of expressing time response, however, are used by various investigators for specific reasons. In seawater, the time response decreased with increasing concentration until

it reached a minimum level of 11, 10, and 5 minutes in 35-, 20-, and 5-ppt salinity, respectively. The average value in freshwater at 25° C was approximately 32 minutes.

TABLE 4. RESPONSE TIMES FOR THE ORION CALCIUM ION ELECTRODE

	Response time		
	$T_{95}(I)$	$T_{95}(E)$	T_1[a]
Freshwater			
25°C - #1	39.5	24.6	23.6(49.9)
#2	47.2	31.3	35.5(65.4)
#3	53.6	65.7	40.8(49.1)
#4	61.1	75.4	29.6(66.8)
#5	47.9	53.4	27.6(----)
10°C - #1	51.2	44.6	41.7(42.0)
Seawater			
35-ppt synthetic	36.1	38.7	32.2(15.0)
natural	30.9	52.8	13.8(----)
20-ppt synthetic	45.0	43.2	26.3(28.3)
natural	44.5	53.9	20.1(----)
5-ppt synthetic	31.2	27.3	5.4(22.0)
natural	26.6	46.1	10.1(----)

[a]Values in parentheses are for Evaluation #1.

The responses of the Orion Calcium Ion Electrodes have been plotted in Figures 9-15 as "delta mV" versus time (minutes) in freshwater and seawater. The "delta mV" term is the difference between the initial electrode potential obtained immediately after immersion in the solution and the potential output at time T. In this manner, the electrode response at various concentrations could be easily depicted on one graph. (Bottle numbers in figures correspond to different levels of concentration.)

The response curves in freshwater for both evaluations illustrate a characteristic found in many other sensors, namely a rapid response with a positive overshoot, followed by a slow recovery to a final stable value. The responses in freshwater of the first and second sensor modules are shown for Evaluation #1 in Figures 9 and 10 over a 2-hour period, and for the third replacement module in Figure 11 over a 1-hour period. In most cases, the electrode potentials never actually leveled off, and a constant drift (usually negative) developed sometime after 90 minutes for the first two sensors and after 30 minutes for the third. At 10°C, the first sensors responded about the same as they did at 25°C (see Figure 12), while the

response of the third module was much slower with greater drift and instability at 10°C. (See Figure 13.)

In seawater, all the sensors exhibited the overshoot characteristic similar to the freshwater response curves and had the same problems with negative drifts as observed in freshwater samples. (See Figures 14 and 15.) The results with the second sensor at 20-ppt salinity was typical of the behavior at all salinities in Evaluation #1 and are shown in Figure 14. The results in seawater with the third sensor (Figure 15) were also similar at all salinities, except for a slight decrease in the magnitude of the overshoot behavior. The response of the third module in 35-ppt salinity seawater is shown in Figure 15 and illustrates the peculiar behavior of the large negative drifts in electrode potential in the most concentrated seawater samples (#4). In general, the electrode response in freshwater and seawater was much slower than expected and suffered from continuous drift problems.

DRIFT

The drift of the calcium electrode for each calibration run is summarized in Table 5 for five different time ranges. The "short-term stability" was calculated as the change in the electrode potential over a 15-minute period after the sensor had "stabilized," or had been immersed in the same standard solution for 2 hours. The sample was sealed at all times to prevent concentration changes during the tests, and the results were averaged over the entire calibration run. The drift over a 1-day period was determined from the reading taken 3 hours after sensor immersion and the reading taken the following day in the same solution. The drift over 1 week was determined from the differences between the calibration runs completed 1 week apart in the same standard solutions.

The long-term stability was measured over a 30-day and 50-day period. The 30-day drift was calculated from the average difference between two calibration runs completed 1-month apart in the same standard solutions. The longer 50-day drift test was performed by continuously monitoring the electrode response while it was sealed in a seawater sample maintained at a constant temperature. The long-term drift tests were only performed with the third sensor (30-d test) and the second sensor (50-d test).

The results in Table 5 indicate that in all the runs the first two sensors were more stable than the third sensor in the short-term tests. The daily, weekly, and monthly drift results seem to indicate that most of the electrode drift occurs the first day, after which it begins to level off. The 50-day drift test, however, illustrated in Figure 16, shows that the agreement in electrode potential over a long period of time may simply be gratuitous. Although the initial and final readings may be quite close (3.7 mV in this case), the differences occurring during the test can be high (up to 16.2 mV on day 30). To ensure that the concentration in the sample had not changed during the tests, the calcium concentration was measured before and after the test.

TABLE 5. DRIFT OF THE ORION CALCIUM ION ELECTRODE

Time period	Water type		mV[a]
After 2 hours	FW-25°C -	#1	0.5(0.3)[b]
		#2	0.3(0.2)
		#3	0.6(0.1)
		#4	0.1(0.0)
		#5	0.5(---)
	FW-10°C -	#1	0.8(0.1)
	SW	5 ppt	0.3(0.2)
		20 ppt	0.5(0.3)
		35 ppt	0.6(0.5)
1 day	FW		4.9(4.3)[b]
1 week	FW		6.9(6.0)[b]
1 month	FW		7.5
50 days	SW		3.7(16.2)[c]

[a]Change of 0.2 mV corresponds to an error of 1.5% in concentration.

[b]Values in parentheses are for Evaluation #1. Other values are for Evaluation #2.

[c]Worst case value that occurred on 30th day.

ENVIRONMENTAL EFFECTS

The Orion Calcium Ion Electrode was subjected to variations in ambient light intensity to determine possible deleterious effects of light attenuation (or variations in "turbidity") on the electrode response, as reported by some recent studies.

The effects of light intensity and other environmental conditions (flow and external motion) on the sensors were determined, and the results summarized in Table 6 for Evaluations #1 and #2.

The tests indicate that the sensors are relatively unaffected by variations in ambient light and only slightly affected by external motion of the electrode or connecting wire. The sensors were sensitive, however, to changes in flow around the sensor module (particularly the third module) where the deviations in electrode potential reached as high as $\pm$1.7 mV.

TABLE 6. ENVIRONMENTAL EFFECTS ON THE ORION CALCIUM SENSOR[a]

Parameter	Evaluation #1	Evaluation #2
Light (low and high)	0.0	0.1
Flow	±0.5	±1.7
External motion	±0.3	±0.3

[a]Change in mV after parameter was applied.

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APPENDIX - INSTRUMENT THEORY

The Orion Calcium Ion Electrode Model #93-20 consists of a replaceable, pretested sensing module which is activated by screwing the module into the electrode body. The sensing module contains a gelled internal filling solution separated from the sample by an organophilic membrane that is saturated with an organic liquid ion-exchanger contained in a reservoir surrounding the membrane. (See Figure 1.) When the membrane is saturated with the organic liquid ion-exchanger, it is selective for calcium ions and a potential develops across the membrane, the magnitude of which is a function of the amount of calcium ions present in the sample solution. The potential is measured against a constant reference potential generated by the reference electrode. The measured potential (E) corresponds to the level of calcium ion as described by the Nernst equation:

$$E = E^\circ + S \log A \qquad (3)$$

where E° is a constant potential, A is the calcium ion activity, and S is the electrode slope equal to the term RT/zF. At 25°C, the theoretical slope is equal to 29.6 mV/decade, where R is the universal gas constant, T is the temperature (°K), z is the ionic charge (+2 for calcium), and F is Faraday's constant. It is important to note that the activity (A) is not equal to concentration in most aqueous solutions.

The activity of an ion can be thought of as the "effective concentration" of the free ion in solution and is affected by temperature, pressure, ionic interactions (such as ion complexion or ion-pair formation), and ionic strength (a chemical parameter related to the number and charge of all the ions in the solution). The activity (A) is equal to the product of the ionic "activity coefficient," γ_+, and the total concentration of the ion, m:

$$A = \gamma_+ m_+ \qquad (4)$$

where γ_+ is a function of ionic strength (I) and various ionic interactions.

Regardless of the electrode's "specificity" for the ion desired, the sensor response can only be affected by the free ionic activity, not the total concentration. Since many chemical species in natural waters are partially "tied up" by complexation with other ions or by adsorption on particulate matter, a large fraction of some elements may not be detected by these sensors.

Ideally, the electrode pair would be calibrated with standard solutions of known activity and the electrode potential would be fitted to the Nernst equation previously given. In this case, a plot of E (in millivolts), versus the logarithm of the ionic activity, would have a slope equal to the Nernst slope (2.3 RT/zF) and the intercept equal to E°. The activity coefficients, however, can only be determined for salts and not for ionic species. For example, although the γ_+ for the potassium ion - (K+) can only be estimated by splitting the $\gamma_\pm$ (KCl) into its ionic components according to some arbitrary convention. One of the most common methods in use today for splitting activity coefficients into ionic components is the McInnes

Convention, by which it is assumed that $\gamma_+(K^+) = \gamma_-(Cl^-)$. Since this is only an arbitrary convention, it is obvious that the γ_+ for an ionic species cannot be determined absolutely, even in pure water.

In natural waters, the situation is much worse due to the presence of many other ions in the solution, all of which affect the value of γ_+ to a certain extent. To circumvent this problem, a "working curve" can be established for sensors in natural waters in which the electrode potential is determined as a function of the logarithm of concentration of the desired ion. Since the values of γ_+ (ion) are not known, the electrodes must be calibrated in standard solutions, which not only contain known concentrations of the desired ion, but also duplicate the background "matrix effects" of the ions in the sample. In this situation, the activity of the ion is the same in both the standard and the sample, and a reliable calibration curve can be prepared in terms of concentration. An electrode measurement in seawater, therefore, requires the calibration of the sensor in standard seawater solutions that contain not only a known concentration of the desired ion, but also a background matrix which simulates the composition of the samples as closely as possible.

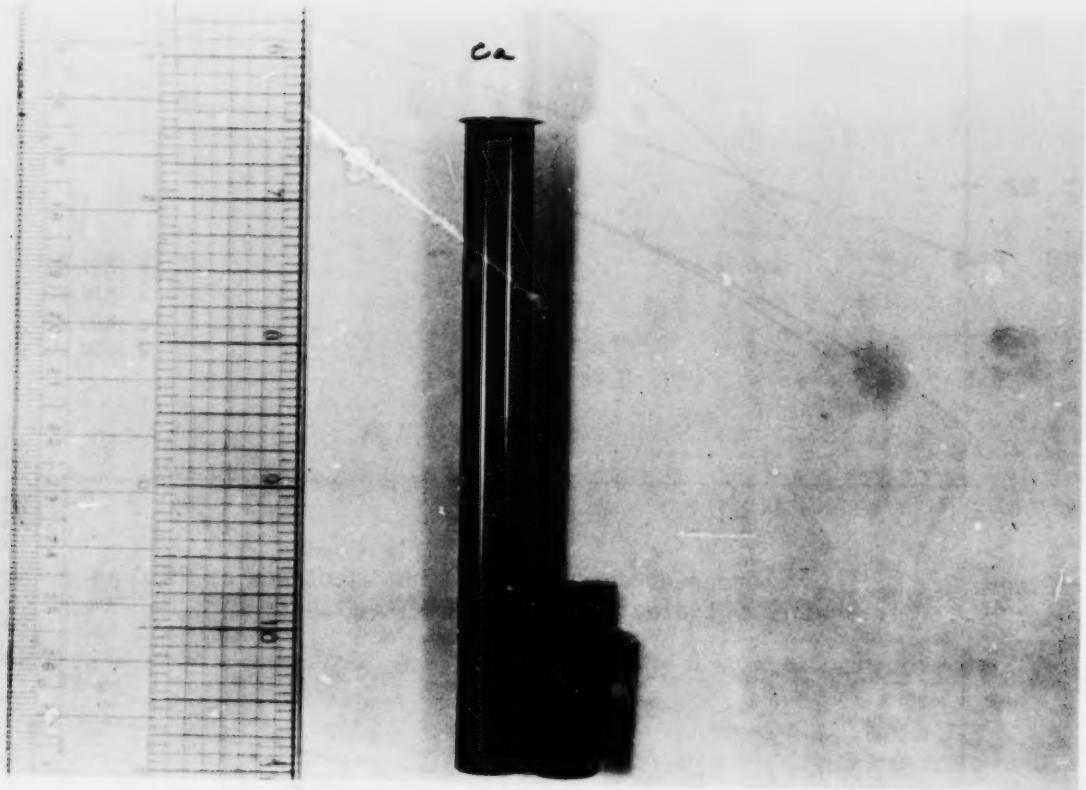

Figure 1. Sensor module for the Orion #93-20 Calcium Ion Electrode.

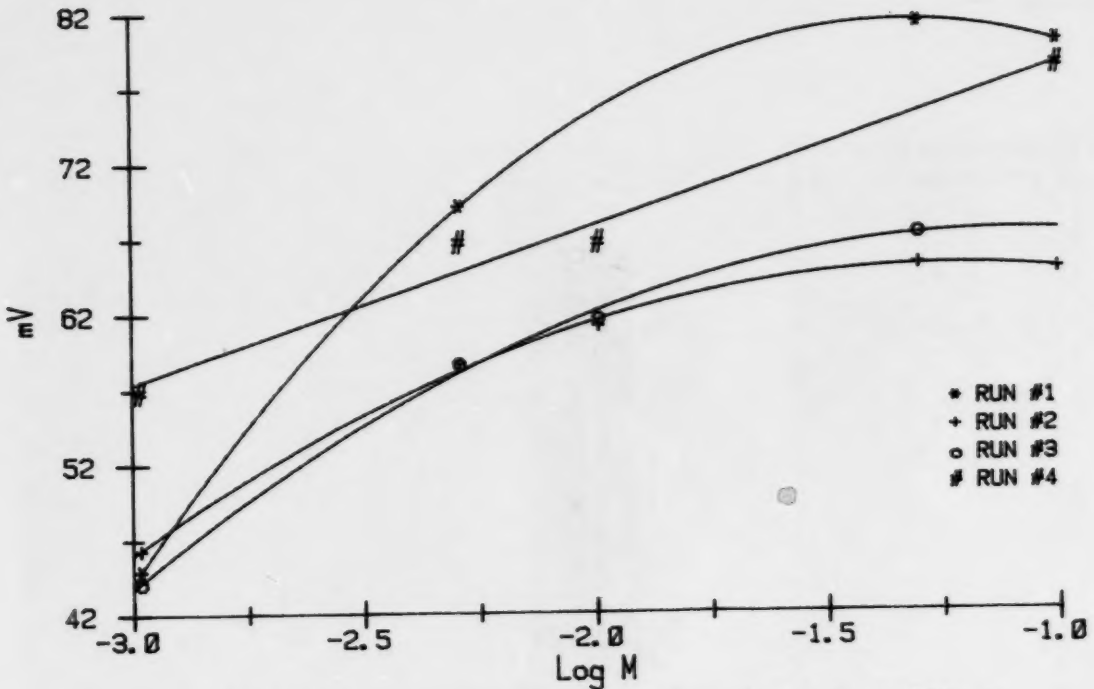

Figure 2. Calibration curves for Orion calcium electrode at 25°C in freshwater - Evaluation #1.

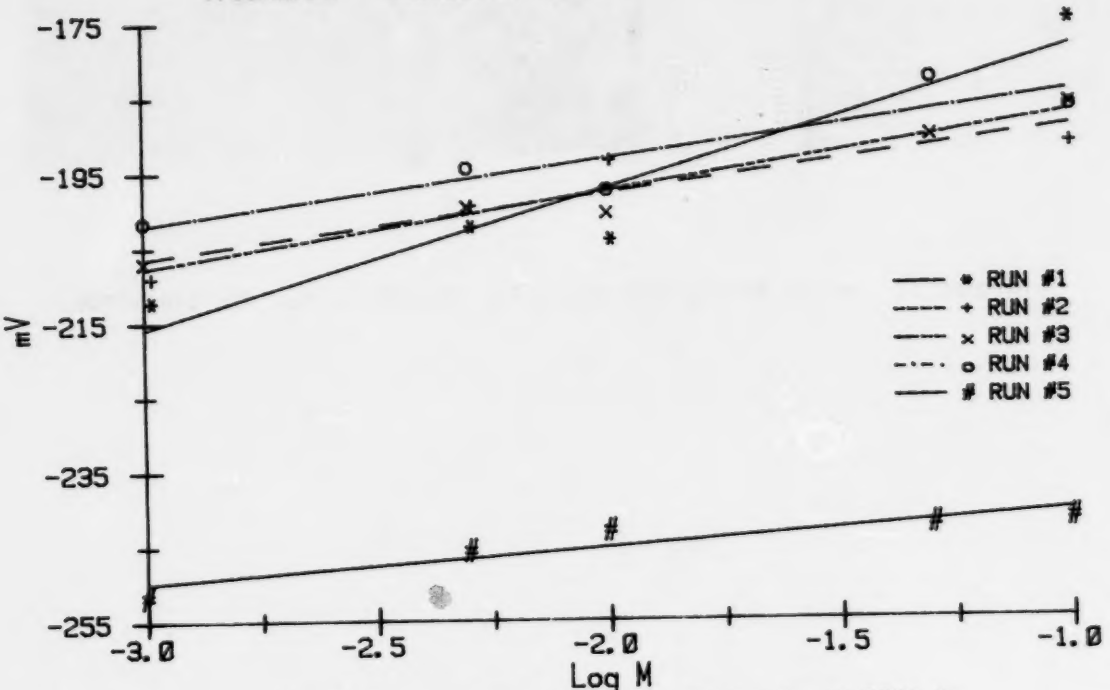

Figure 3. Calibration for Orion calcium electrode at 25°C in freshwater - Evaluation #2.

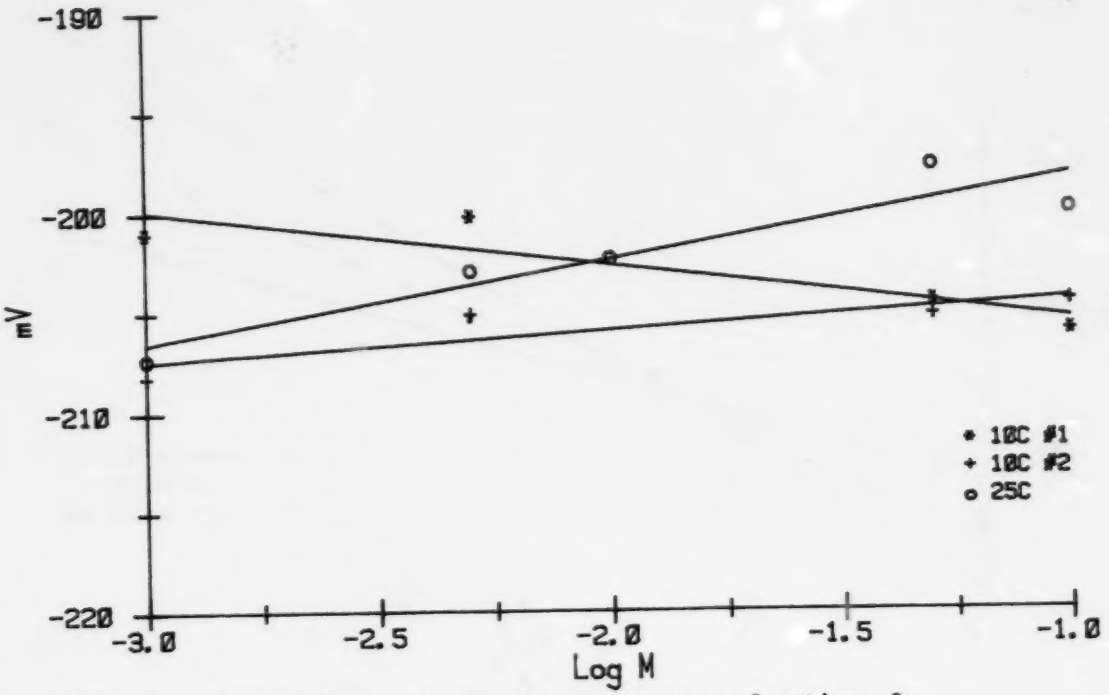

Figure 4. Orion calcium electrode response as a function of temperature and concentration in freshwater - Evaluation #3.

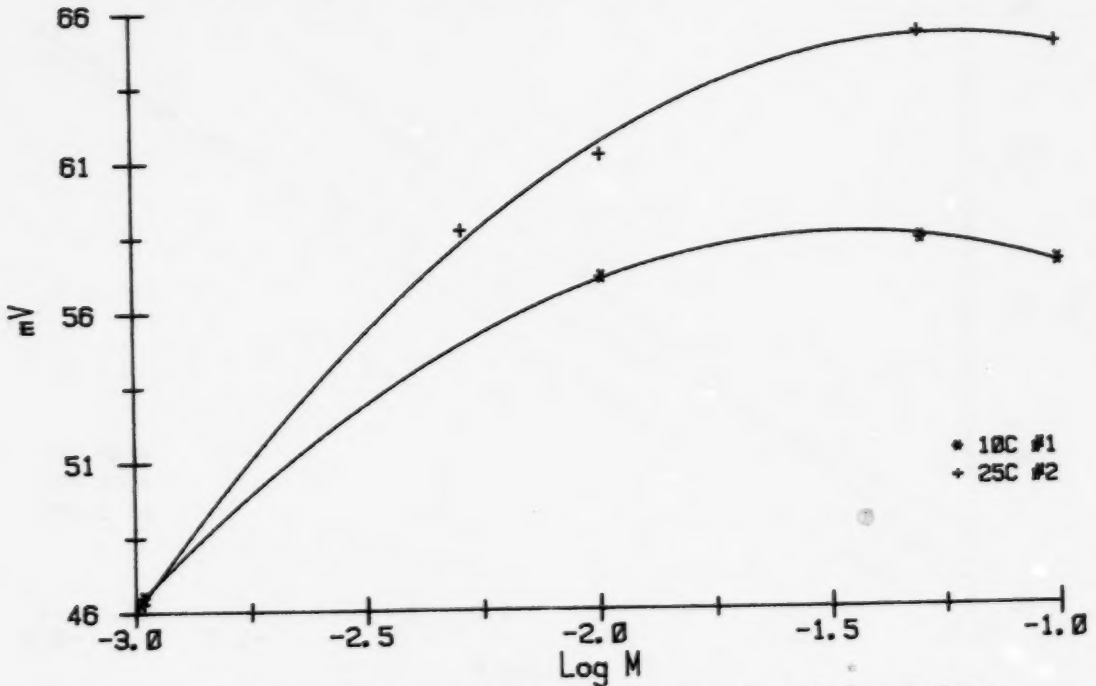

Figure 5. Calcium electrode response as a function of temperature and concentration in freshwater - Evaluation #1.

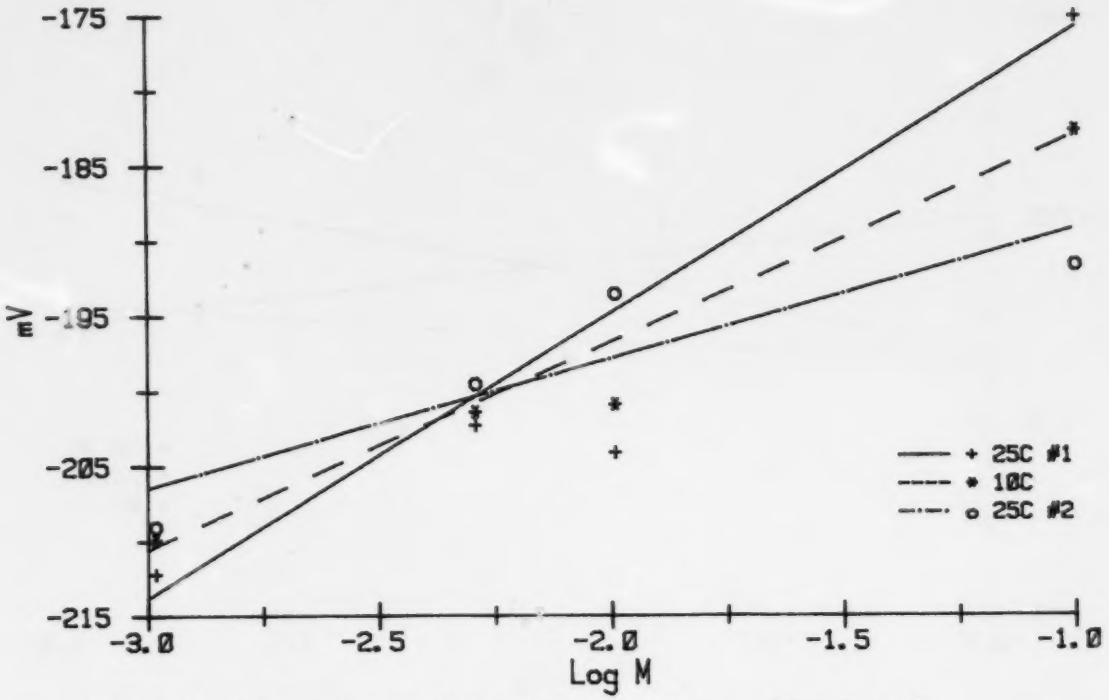

Figure 6. Orion calcium electrode response as a function of concentration at 10°C and 25°C - Evaluation #2.

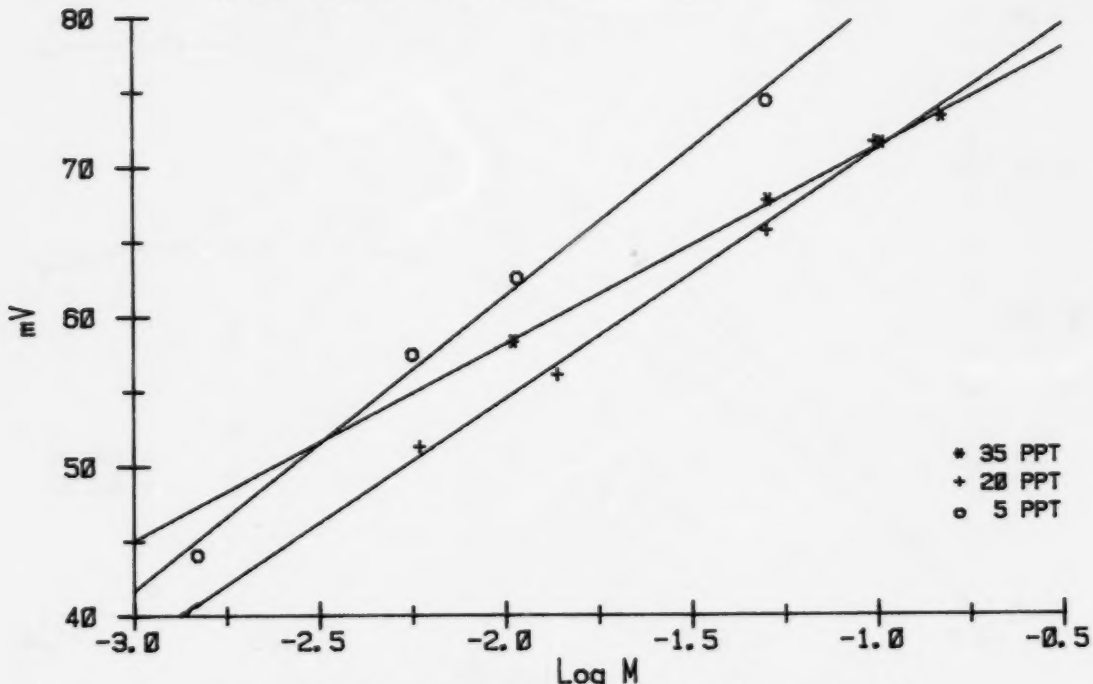

Figure 7. Evaluation #1 - Orion calcium electrode response in 35-, 20-, and 5-ppt salinity seawater at 25°C.

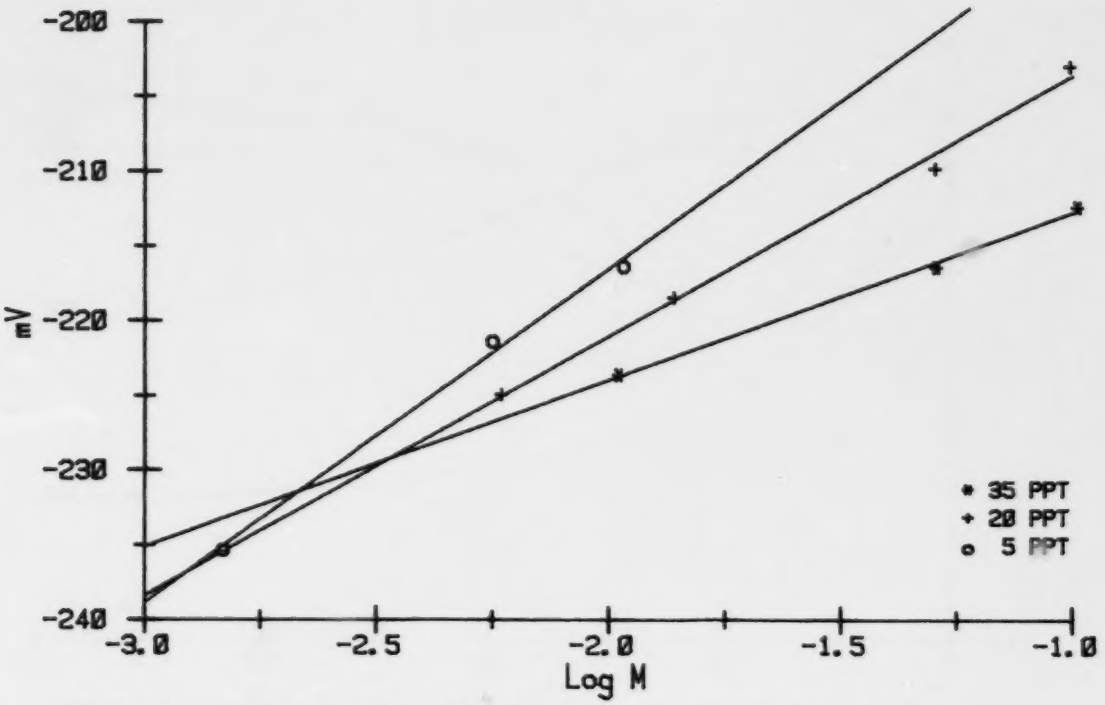

Figure 8. Evaluation #2 - Calcium electrode response as a function of Ca^{2+} concentration in 25-, 20-, and 5-ppt salinity seawater.

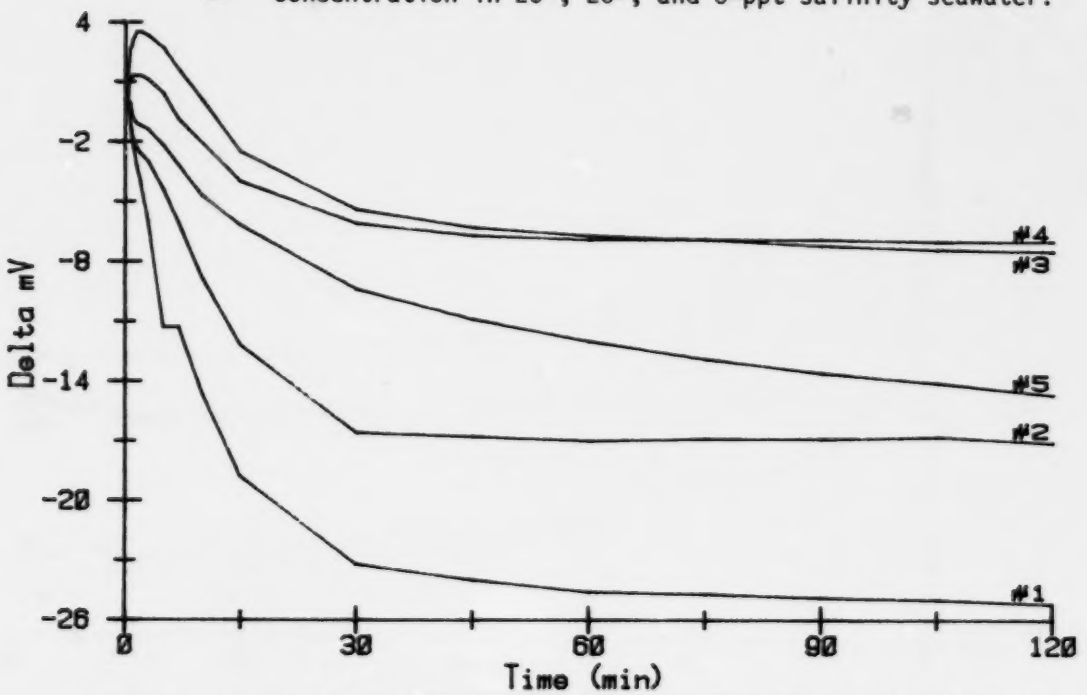

Figure 9. Time response of the Orion Calcium Ion Electrode #93-20 in freshwater at 25°C - Run #1, Evaluation #1.

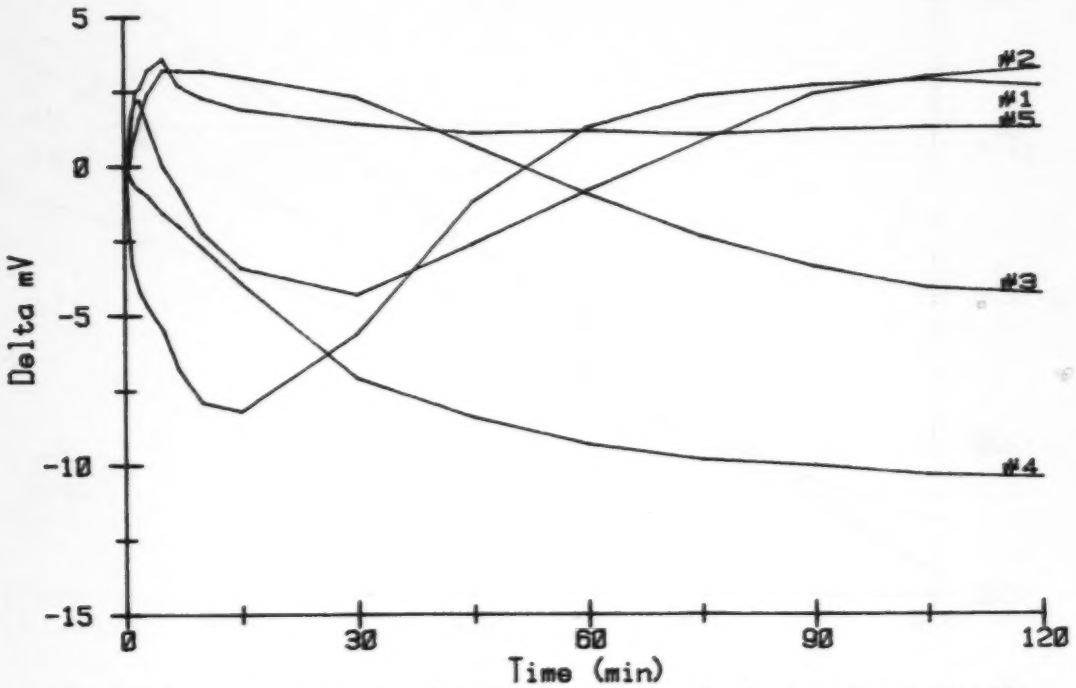

Figure 10. Time response of the Orion electrode in freshwater at 25°C - Run #4, Evaluation #1.

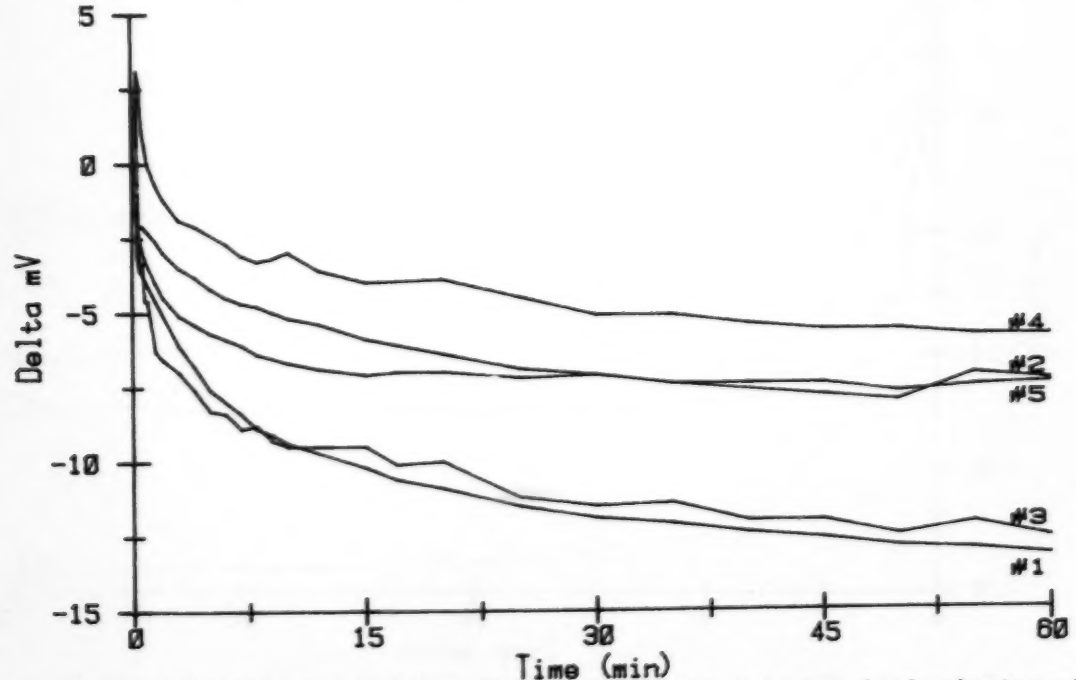

Figure 11. Time response of the Orion calcium electrode in freshwater at 25°C - Run #4, Evaluation #2.

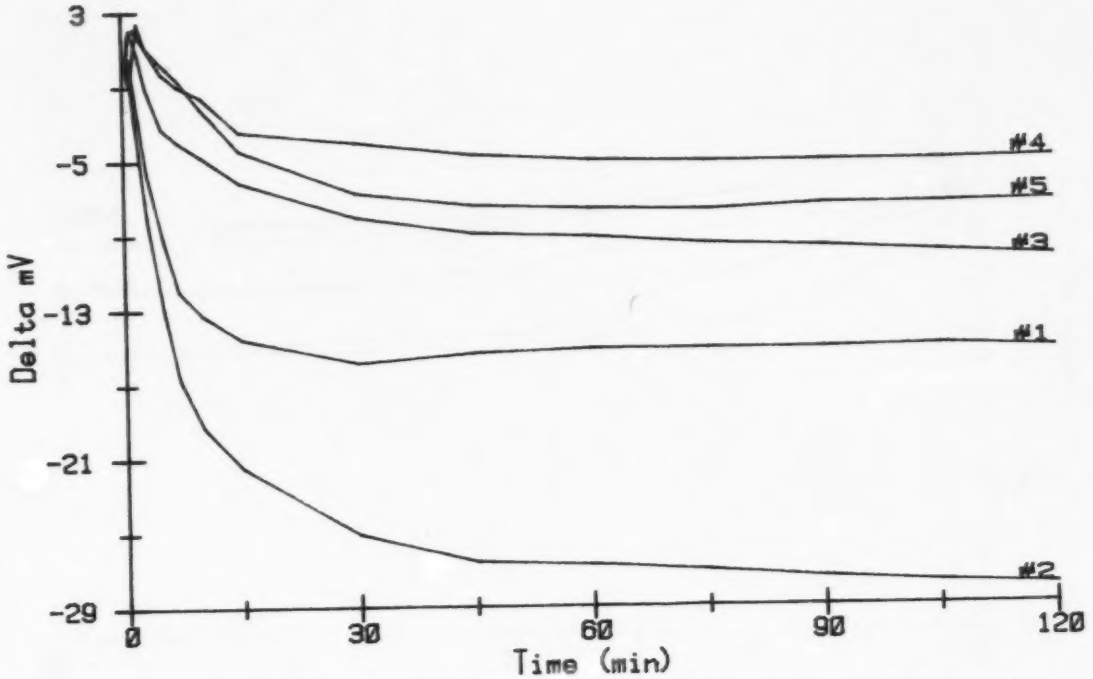

Figure 12. Electrode response as a function of time and concentration in freshwater at 10°C - Evaluation #1.

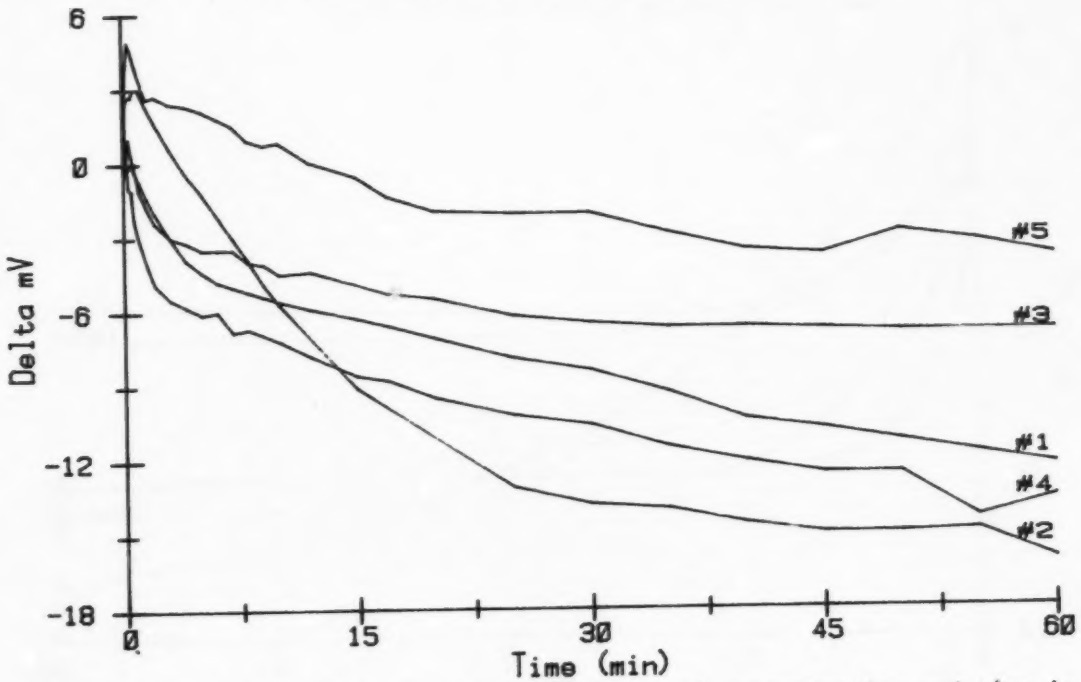

Figure 13. Electrode response as a function of concentration and time in freshwater at 10°C - Evaluation #2.

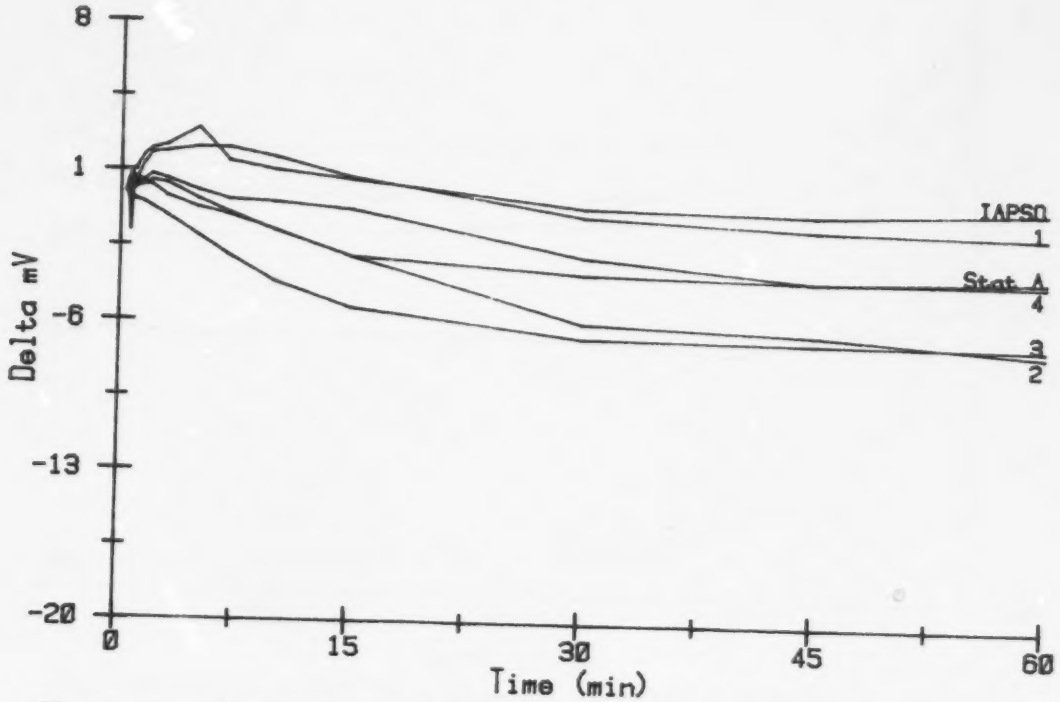

Figure 14. Time response of the Orion calcium electrode in 20-ppt salinity seawater - Evaluation #1.

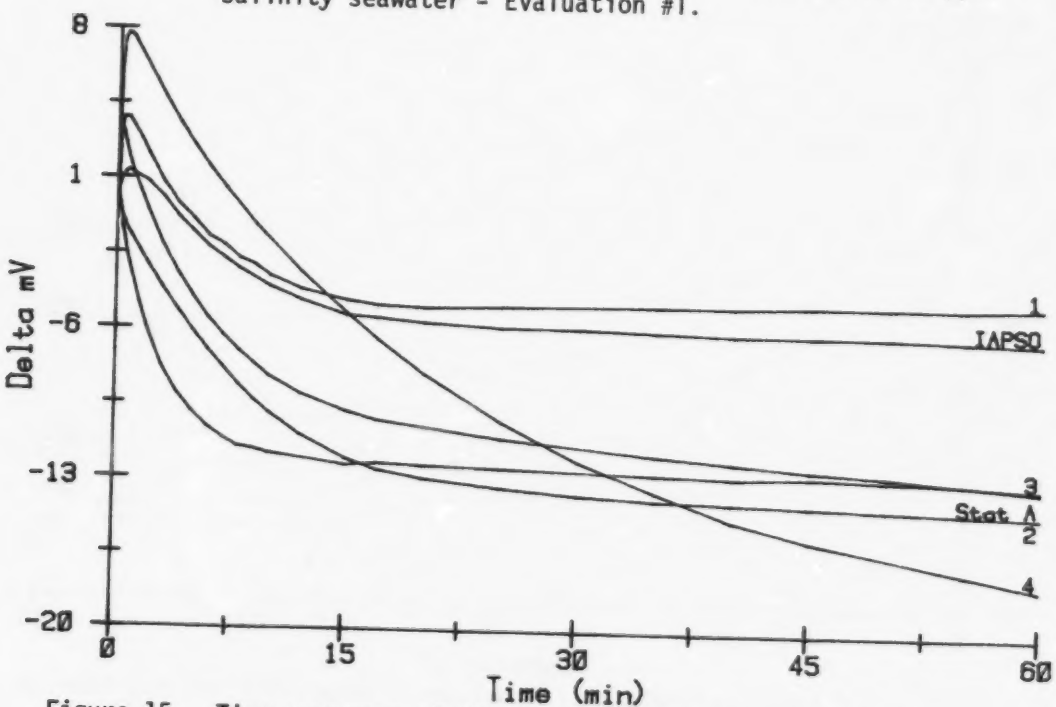

Figure 15. Time response of the Orion calcium electrode in 35-ppt salinity seawater - Evaluation #2.

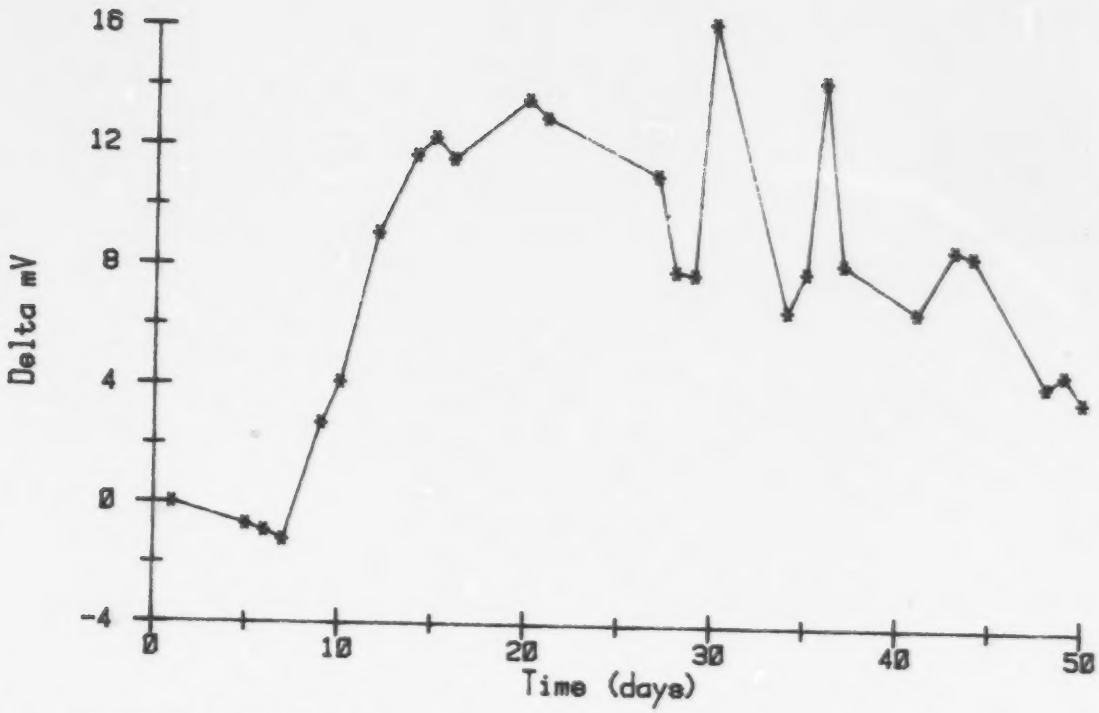

Figure 16. Drift in electrode potential at 25°C over a 50-day period at constant calcium concentration.